Chapter 1

Magnetic Properties of the DNA-Quaternary Ammonium Surfactant Complexes Studied by EMR spectroscopy and SQUID Measurement

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14. ABSTRACT

It is so well established that DNAs are the most important molecules in living cells storing genetic and hereditary information and they have been and still are the center of biological science. On the other hand, due to their unique chemical structures and versatile functionalities associated with their structural characteristics many research groups are studying the materials science aspects of natural and18 synthetic DNA. In particular, recent explosive, scientific and technological interest in nanoscience and nanotechnology is accelerating the exploration of DNA natural and synthetic, for various properties such as electrical conductivity electron or hole transport and optical properties. In contrast, study on the magnetic properties of DNA is still in the infant stage, although there were some reports on electron spin resonance spectroscopic (ESR) studies as early as late 1950?s. Recently, we reported for the first time that natural dsDNA in dry state (A-DNA) showed an extremely broad electron magnetic resonance (EMR) signal as well as an S-shaped magnetization-magnetic field (M-H) curve in SQUID measurements. The broad EMR signal was interpreted as a cyclotron resonance (CR), which is possible only when the double helical structure of each dsDNA coherently couples throughout the elementary fibrils resulting in the formation of lateral loop currents responsible for the S-shaped M-H curves in SQUID measurements. Both the EMR signals and the S-shaped magnetizations are found to be strongly correlated to each other. Assuming that the fibrillar dsDNA are in a morphologically heterogeneous structure, formation of such loop currents by the external field must be much more favored in ordered regions than in amorphous ones. In other word, the dsDNA can not only be a molecular solenoid in the single molecular level, but also can be a ferromagnetic in the well ordered regions due to coherently coupled bundles of DNA molecular solenoids. Therefore, if one introduces a magnetic dipole into the DNA molecular solenoid, a strong enhancement of DNA susceptibility is expected to occur as in an electrical solenoid with a magnetic bar. In this respect, we tried to insert various stable radicals into the dsDNA and succeeded in observing strong enhancements in their magnetic susceptibilities.

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1.1 Introduction

It is so well established that DNAs are the most important molecules in living cells storing genetic and hereditary information and they have been and still are the center of biological science. On the other hand, due to their unique chemical structures and versatile functionalities associated with their structural characteristics many research groups are studying the materials science aspects of natural and synthetic DNA. In particular, recent explosive, scientific and technological interest in nanoscience and nanotechnology[1–27] is accelerating the exploration of DNA, natural and synthetic, for various properties such as electrical conductivity[28–32], electron or hole transport[33–50] and optical properties[51–64]. In contrast, study on the magnetic properties[65–80] of DNA is still in the infant stage, although there were some reports on electron spin resonance spectroscopic (ESR) studies as early as late 1950's[65–68]. Recently, we[78] reported for the first time that natural dsDNA in dry state (A-DNA) showed an extremely broad electron magnetic resonance (EMR) signal as well as an S-shaped magnetization-magnetic field (M-H) curve in SQUID measurements. The broad EMR signal[76,78,79] was interpreted as a cyclotron resonance (CR), which is possible only when the double helical structure of each dsDNA coherently couples throughout the elementary fibrils resulting in the formation of lateral loop currents responsible for the S-shaped M-H curves in SQUID measurements. Both the EMR signals and the S-shaped magnetizations are found to be strongly correlated to each other. Assuming that the fibrillar dsDNA are in a morphologically heterogeneous structure, formation of such loop currents by the external field must be much more favored in ordered regions than in amorphous ones. In other word, the dsDNA can not only be a molecular solenoid in the single molecular level, but also can be a ferromagnetic in the well ordered regions due to coherently coupled bundles of DNA molecular solenoids. Therefore, if one introduces a magnetic dipole into the DNA molecular solenoid, a strong enhancement of DNA susceptibility is expected to occur as in an electrical solenoid with a magnetic bar. In this respect, we tried to insert various stable radicals into the dsDNA and succeeded in observing strong enhancements in their magnetic susceptibilities[79].

Since the loop current is driven in the well ordered regions of dsDNA by constructive lateral interferences of cyclotron motion of charge carriers along the helical π-way of dsDNA molecular axis, if one increases the distance between dsDNA molecules, the coherent coupling of the cyclotron motion between them is expected to weaken, which would bring about a simultaneous diminish in the intensity of the extremely broad EMR signal and the magnitude of the S-shaped M-H curve. In this work, therefore, we prepared DNA-quaternary ammonium (Q^+) surfactant complexes bearing finite length of alkyl groups to study the influence of the lateral distance of DNA molecules on the broad EMR signal and also on the S-shaped

M-H magnetic behavior described above.

1.2 Experimental

1.2.1 Preparation of DNA-Q Complexes

Salmon sperm DNA (0.130 g; 1.0×10^{-7} mol, purchased from Aldrich Chemical) of 2000 base-pairs was dissolved in 100 mL of 0.1M acetate buffer solution (pH 6.8), to which slowly added was 90 mL solution of hexadecyltrimethylammonium (CTMA) bromide (0.165 g; 4.53×10^{-4}mol, purchased from Aldrich Chemical). The whole mixture was stirred gently two more hours at room temperature. The precipitate formed was collected on a filter and washed thoroughly with triply distilled water. Finally, the collected DNA-CTMA complex was dired at 40 °C, 5×10^{-2} Torr. The recovered yield was 0.219g (93.2 % of the theoretical value). The DNA-dodecyltrimethylammonium (DTMA) complex was prepared by the exactly same method. The precipitate of DNA-tetramethylammonuim(TMA) complex was obtained by adding cold ethanol(ethanol:DNA-TMA solution=4:1) into the DNA-TMA complex solution. DNA-TMA complex was washed thoroughly with absolute ethanol. The DNA-CTMA-PTMI complex was prepared by the following method; Dry DNA (0.13 g) was dissolved in 100 mL volumetric flask in acetate solution for 24 hours under protection by an aluminium foil. Separately, 3.3 mg (1.52×10^{-5} mol) of PTMI (4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy) was dissolved in 50 mL anhydrous ethanol using a volumetric flask. 1.32 mL of PTMI solution was poured into 20 mL DNA buffer solution and slowly stirred for 24 hours at room temperature. The DNA-PTMI was precipitated by adding four times of cold ethanol. The DNA-PTMI complex was washed by cold ethanol and then dissolved in 0.1 M acetate buffer solution. DNA-CTMA-PTMI complex was prepared with DNA-PTMI solution by adding equivalent amount of CTMA solution into the DNA-PTMI 0.1M acetate buffer solution. The DNA-CTMA-PTMI complex was collected on a filter and dried in vacuum 5×10^{-2} Torr at 40 °C.

The DNA-CTMA(1M) and DNA-CTMA(0.3M) were prepared from DNAs provided by Prof. N. Ogata's group. We used 2 different lengths of DNAs(molecular weight of 1.0×10^{6}(1 M) with 1538 base-pairs and 3.0×10^{5}(0.3 M) with 923 base-pairs). DNAs were dissolved in distilled water and then surfactant solution was mixed with the DNA solution over 2 hours. The DNA-surfactant complexes were washed in distilled water, followed by filtration and drying process in a vacuum oven for 24 hours at 40 °C, 5×10^{-2} Torr.

1.2.2 Instrumentation

X-Ray diffractograms of the DNA^{-}-Q^{+} complexes were obtained by using a synchrotron radiation (1.542 Å) of the Synchrotron Lab, Pohang Technological University, Pohang, Korea. CD/ORD spectra of natural DNA and the DNA-CTMA complex solutions (pH = 6.8 acetate buffer, conc.: 5.0×10^{-7} M) were measured

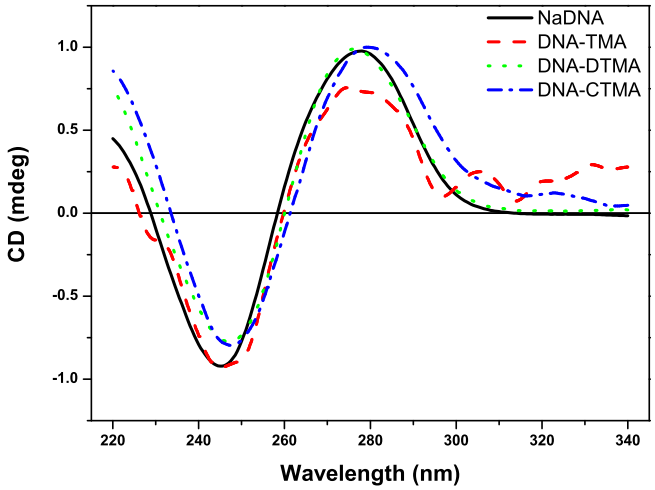


Figure 1.1 CD/ORD spectra of NaDNA, DNA-TMA, DNA-DTMA and DNA-CTMA complexes

under nitrogen atmosphere on a J20 spectropolarimeter (JASCO, Japan) over the 220 - 340 nm wavelength range. The spectra of the other two complexes were obtained in ethanol solution under nitrogen atmosphere. Raman spectra of complexes powders were collected at room temperature on a LabRam HR (Jobin-Yvon, France) at the excitation wavelength of 514.5 nm with intensity of 0.5 mW. The detailed procedure for the measurements of EMR signals of the samples was the same as previously described[76,78–80]. Since the presence of adsorbed water and oxygen molecules was found to result in erroneous EMR signals, it was made sure that we removed the two chemical species as specified in the earlier paper[76,78–80].

1.3 Results and Discussion

1.3.1 Structure of DNA-Q Complexes

The CD spectra of the complexes are shown in Figure 1.1 together with the spectrum of natural DNA. They are basically the same, although only the spectra of natural DNA and DNA-TMA complex were obtained in an acetate buffer (pH = 6.8, 5.0×10^{-7} M) whereas the other two in ethanol solution. The spectrum of the natural DNA is in an excellent accord with those reported for B-dsDNAs in literature[81]. The fact that the CD spectra of the present DNA^{-}-$CTMA^{+}$ salts or complexes as shown in Figure 1.1 are very similar to that of the natural, double strand DNA (dsDNA sample) strongly indicates that all the complexes also are in the double stranded conformation. Moreover, the minima, maxima and zero CD wavelength position shifts slightly toward to longer wavelength side as we increased the length

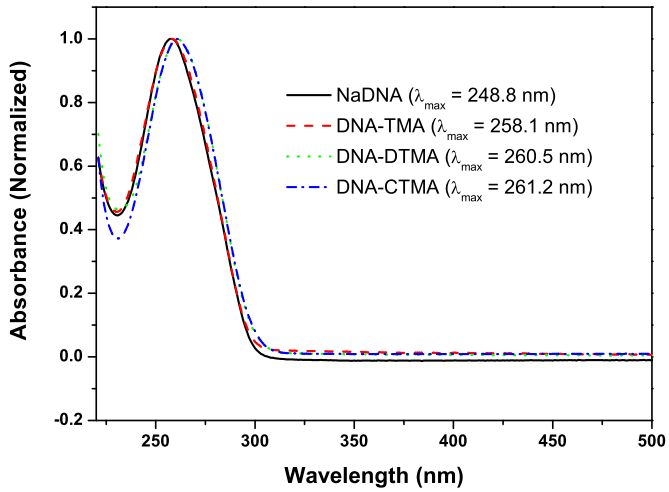
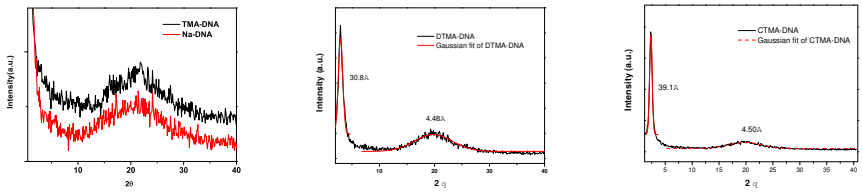


Figure 1.2 UV-Visible spectra of NaDNA, DNA-TMA, DNA-DTMA, and DNA-CTMA complexes

of the alkyl group in the Q^+ group, which parallels the slight red-shift observed for UV-absorption positions (Figure 1.2) of the complexes. Figure 1.2 clearly demonstrates that the λ_{max} absorption position increases from 258 nm for the natural DNA sample to 261.5 nm for DNA-CTMA complexes. We note the exactly same trend in their CD spectra: the longer the alkyl chain in the quaternary ammonium part, the more the CD spectral position moves toward the longer wavelength side. In short, The CD spectra are nicely compared with UV-absorption spectra (Figure 1.2) of the complexes. In fact, their λ_{max} positions in UV-absorption spectra coincide very well with their zero CD wavelengths (258.1, 260.0, 261.5 nm respectively), as they should do. It, however, should be noted that CD as well as UV-absorption characteristics of the complexes depend only to a minor extent on the length of the alkyl group in the quaternary ammonium group. This can be taken as a strong implication that original structure in solution of the natural dsDNA is disturbed only slightly by changing the Na^+ ion with the $CTMA^+$ ions and other Qs^+.

Figure 1.3 compares the X-ray diffractograms of the natural DNA sample, DNA^--TMA^+, DNA^--$DTMA^+$ and DNA^--$CTMA^+$ complex: both samples of long alkyl groups commonly reveal a very broad, weak diffraction centered at about $2\theta = 20°$. But only DNA-CTMA complex shows a sharp peak at $2\theta = 2.3°$. Diffraction angle of $2\theta = 19.7°$ corresponds to the spacing of 4.5 Å, whereas $2\theta = 2.3°$ corresponds to the spacings of 39.1 Å. The natural DNA and DNA^--TMA^+ appear to be amorphous and did not show any diffraction in the small angle region. A close examination of X-ray diffractograms (Figure 1.3) of the complexes reveals an inter-



(a) (b) (c)

Figure 1.3 X-ray diffractograms of (a)natural DNA and DNA-TMA,(b)DNA-DTMA and (c) DNA-CTMA complex

esting dependence of the Q^+-DNA^- complexes on the length of the alkyl groups in the Q^+ part. The sharp small angle diffractions teach us that the DNA-CTMA complex forms a layered morphology even when the samples were not subjected to any mechanical or field-induced organization and alignment of the molecular chains. The long spacing, i.e., the interlayer distance, estimated from the diffraction patterns, is 39.1 Å. This number is significantly smaller than theoretically estimated layer thickness value of 60 Å for the DNA-CTMA, assuming that the diameter of the B-form DNA core is 20 Å as reported and 20.0 Å for the hexadecyl ammonium structure where the alkyl group was hypothesized to be in the trans extended conformation. The reduced layer thickness can be ascribed to two different possibilities: conformational irregularity in the alkyl group and partial intercalation between the alkyl group originated from the adjacent $CTMA^+$ group. It is very possible that the two factors together cause a reduction of interlayer distance. This morpholocal picture is in complete accord with those reported by Okahata et al[32]. and Ogata et al.[53,55]. We, however, believe that the layered structures are in fluid state because their wide-angle diffractions are very broad (peak width at the half-maximum: 2θ = 6-7°) and weak. Another important fact is that the natural DNA did not show any small-angle diffraction, suggesting that they do not form layered structures, although it appears to be in liquid crystalline (nematic) state when examined through a polarizing microscope. Similar observations were made for the DNA-TMA salt, see Figure 1.3(a).

1.3.2 Magnetic properties

1.3.2.1 SQUID measurements

Among the three DNA^--Q^+ complexes we studied only the magnetic properties of DNA-CTMA. The preliminary studied showed as that the DNA-DTMA complex revealed the magnetic properties very similar to those of DNA-CTMA, whereas DNA-TMA's magnetic properties were not much different from natural DNA's. Figure 1.4 shows a magnetization-magnetic (M-H) field curves obtained for DNA-CTMAs, and CTAB(hexadecyltrimethylammonium bromide). In order to use diamagnetic reference for SQUID magnetometer, we also measured M-H curve for

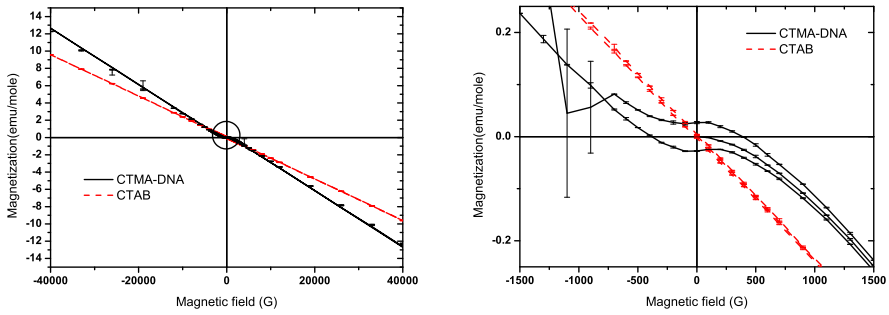


Figure 1.4 (a)Magnetization (M)-magnetic field (H)hysteresis obtained for DNA-CTMAs and DNA-CTMA-PTMI. (b)Expanded plots from 0 to ± 1500 G.

CTAB which is one of parent molecules of DNA-CTMA. As one can see in Figure 1.4, the diamagnetic response of the CTAB molecule is evident from a negative linear slope over the whole magnetic field range measured. Apart from this, every sample specimens bearing DNA show two distinct M-H responses to the applied the magnetic fields. Below ±3000 G, the M-H patterns clearly show hysteresis behavior with ±500∼1000 G of the coercive field and ±0.02∼0.04 μ_B of the remnant magnetization, whereas CTAB does not. However, such hysteresis disappeared above 3000 G. The hysteresis behavior was observed only for the A-DNA and the modified DNA. Therefore, it is conjectured that a certain type of magnetic interaction involving DNA molecules may be responsible for the low-field hysteresis observed. As a consequence, we decided to perform χ-T measurements at two different external magnetic fields, 1000 and 10000 G.

Figure 1.5 shows the χ-T plots obtained for the surfactant modified DNAs. Firstly, the susceptibility values for the DNA-CTMA are three times smaller than that for the A-DNA reported previously by us[78]. Secondly, any enhancement of magnetic susceptibility by free radical intercalation is not observed for the DNA^--Q^+ samples, which is a sharp contrast to the case of the A-DNA. Thirdly, the susceptibility values are always higher for 1000 G than those for 10000 G. For the purpose of better understanding of their intrinsic characteristics more clearly, we considered the total magnetic susceptibility as results of superposition of three different types of susceptibilities as follows:

$$\chi_{tot} = \chi^{dia} + \chi^{Curie} + \chi^{Pauli}, \tag{1.1}$$

where χ^{dia} is the temperature-independent negative molecular diamagnetic susceptibility and χ^{Curie} the paramagnetic Curie susceptibility caused by a localized spins and known to be reciprocally proportional to temperature, and the last temperature-independent χ^{Pauli} is the Pauli spin susceptibility attributed by delocalized conductive spin species. The molar susceptibilities corrected for the molecular dia-

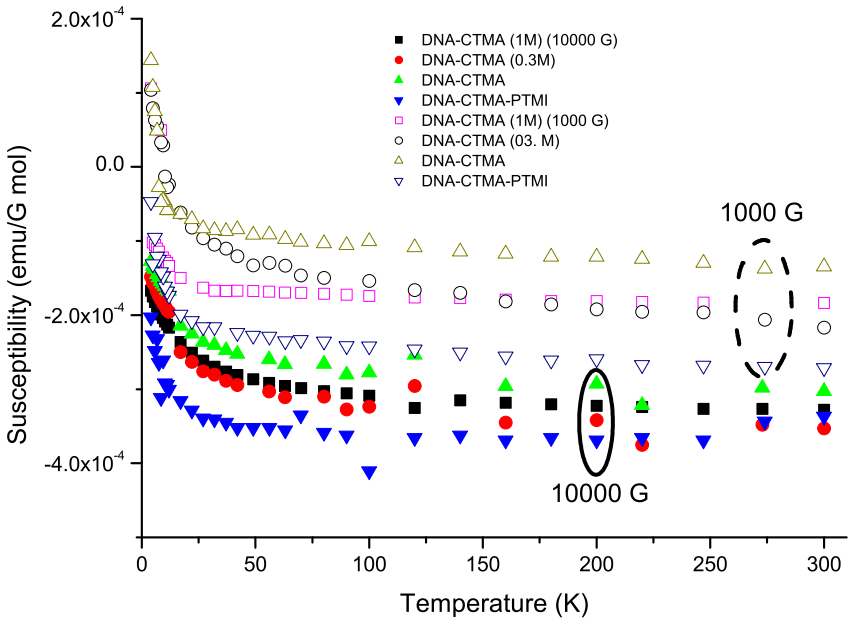


Figure 1.5 Magnetization (M)-magnetic field (H)curves for DNA-CTMA and DNA-CTMA-PTMI obtained at room temperature.

magnetism, χ_m, therefore, can be written as

$$\chi_m(T) = \chi^{Curie} + \chi^{Pauli} = C/T + \chi^{Pauli}. \tag{1.2}$$

The measured DNA-CTMAs' susceptibilities were firstly corrected for the molecular diamagnetic contributions from DNA and CTMA. To this end, a direct M-H response was measured for the CTAB parent molecule at room temperature. As shown in Figure 1.4, the M-H curve is perfectly linear with a negative slope, indicating a clear diamagnetic response of the CTAB molecule. From a linear diamagnetic fitting to the M-H curve, -2.39$\times 10^{-4}$ emu/G·mol of negative slope was obtained. Because CTAB loose one Br^- ion in the process of being attached to the backbone of DNA molecules, a diamagnetic contribution of the Br^- ions should be ruled out in DNA-CTMA. Finally, we obtain -2.05$\times 10^{-4}$ emu/G·mol of the diamagnetic susceptibility for CTMA. When the χ_m versus T with the diamagnetic corrections was fitted to Eq. 1.2, the Curie constant and the Pauli susceptibilities were obtained. Because the susceptibilities at 10000 G were 1.68($\pm$ 0.11) $\times 10^{-4}$ emu/G $\cdot$ mol and can not be discriminated from each other, we listed only the susceptibility values at 1000 G in Table 1.1. The Pauli susceptibilities at 1000 G are twice those for 10000 G. Interestingly, the Curie constant of 9.49$\times 10^{-4}$ emu/G $\cdot$ mol and the Pauli susceptibility of 3.0$\times 10^{-4}$ emu/G $\cdot$ mol for the DNA-CTMA-PTMI are not larger than the average value of 10.1$\times 10^{-4}$ emu/G $\cdot$ mol and 3.08$\times 10^{-4}$ emu/G

Table 1.1 Curie constant and Pauli susceptibilities at 1000 G fitted to Eq. 1.2.

	Curie constant (emu/G · mol) ($\times 10^{-4}$)	χ^{Pauli}(emu/G · mol) ($\times 10^{-4}$)
DNA-CTMA (1 M)	5.62($\pm$ 0.03)	2.85($\pm$ 0.001)
DNA-CTMA (0.3 M)	14.3($\pm$ 0.2)	2.89($\pm$ 0.01)
DNA-CTMA	10.4($\pm$ 0.1)	3.49($\pm$ 0.008)
DNA-CTMA-PTMI	9.49($\pm$ 0.02)	3.00($\pm$ 0.01)

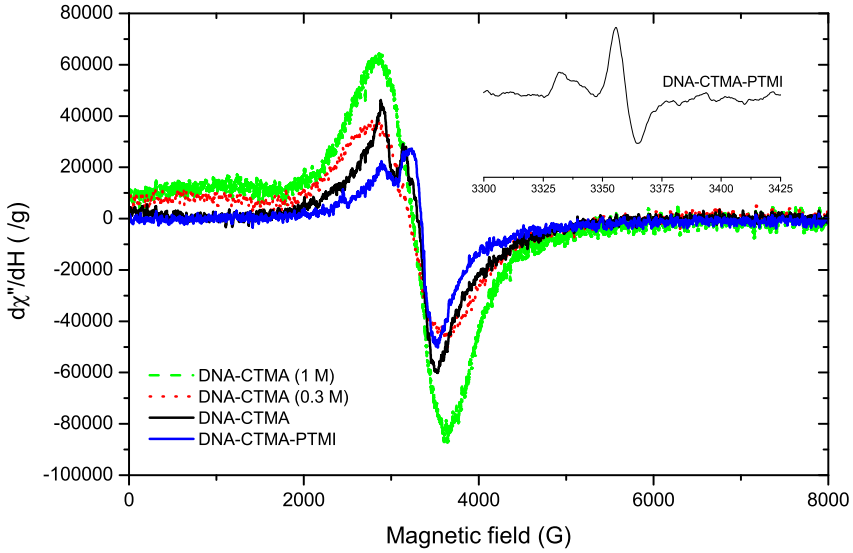


Figure 1.6 Room-temperature EMR spectra obtained for DNA-CTMA and DNA-CTMA-PTMI complexes.

· mol for DNA-CTMA, sharply contrasting to the case of A-DNA-PTMI reported previously[79]. We could not find any regular dependence of the two values on the molecular weight of DNA samples, see Table 1.1.

1.3.2.2 Electron Magnetic Resonance Spectroscopy

Figure 1.6 shows the electron magnetic resonance spectra obtained for DNA-CTMA and DNA-CTMA-PTMI complexes at room temperature. At a first glance, all the spectra show single line with a peak-to-peak linewidth of $\sim$ 1000 G centered at 3300 G, which is completely different from the case of the pristine A-DNA where the EMR spectrum consisted of two distinct signals. There is no molecular weight dependence of EMR lineshapes between DNA-CTMA (1 M) and DNA-CTMA (0.3 M). The most prominent contrast is that there is no the extremely broad EMR signal

corresponding to the cyclotron resonance[82] coupled inductively in the perpendicular direction of the long axis of DNA. Since the interduplex distance is increased by the presence of CTMA molecules, the lateral interference effect of the DNA-CTMA is expected to be less efficient than that of A-DNA. Such effect seems to be reflected in the diminishing intensity of the broad EMR line. For the case of DNA-CTMA-PTMI, an incorporation of the PTMI radical into DNA successfully lead to a spin triplet state as shown in the inset in Figure 1.6. The triplet EMR signal strongly supports the presence of ferromagnetic spin interaction between the PTMI radicals even if their separation is too distant to interact directly with each others. However, the absence of the extremely broad EMR line and the EMR line shape at 3300 G are very similar as for DNA-CTMAs. Considering the absense of any enhancement of the Pauli susceptibility for the DNA-CTMA-PTMI in the χ_m-T graph shown in Figure 1.5 and Table 1.1, it is conjectured that any enhancement of the Pauli susceptibility can not occur if there is no coherent lateral coupling of the cyclotron motion despite the intercalation of the PTMI radicals in DNA giving rise to the spin triplet state in the single molecular level.

Every magnetic phenomenon can be explained by considering an intrinsic spin and/or an orbital motion of charge carriers. Here, the spin magnetism is due to the presence of the nonzero spin magnetic moments parallel to the applied magnetic field, and the orbital magnetism is caused by a circular orbital motion of the charge carrier. As we can see in Figure 1.5, susceptibility value remain almost constant over the wide temperature range. As described before, the helical charge transport makes DNA to behave as a molecular solenoid, that is to say, molecular inductor. Here, it is worthy of mentioning that the helical charge transport can be more efficient under a magnetic field applied in appropriate direction. Moreover, the applied magnetic field can also make the helical charge transport not only to synchronize in same phase but also to interfere in transverse direction, leading to inductive coupling between neighboring DNA molecules. The closer to each other, the stronger the inductive coupling becomes. In other words, the inductive coupling is sensitively influenced by the separation distance between the helices in the transverse direction and also by the presence of impurities hindering coherent helical charge transport. Therefore, the induced magnetic field must be same within a single DNA molecule, but its inductive coupling in the transverse direction depends on the lateral distance between the DNA molecular solenoids. For the case of the A-DNA, the lateral separation is a few Å whereas the DNA-DTMA and DNA-CTMA are at least 4 nm. Accordingly, the lateral inductive coupling is expected to be significantly stronger for A-DNA than for DNA-CTMA, so that the number of DNA molecules participate in the coherently coupled helical charge transport is much larger for A-DNA than for surfactant-DNAs. This implies that the Pauli susceptibility may be the same in both A-DNA and surfactant-DNAs, but magnetization per volume should become smaller with increasing separation distance. Therefore, if a limited amount of impurity is laid in the middle of the helical charge

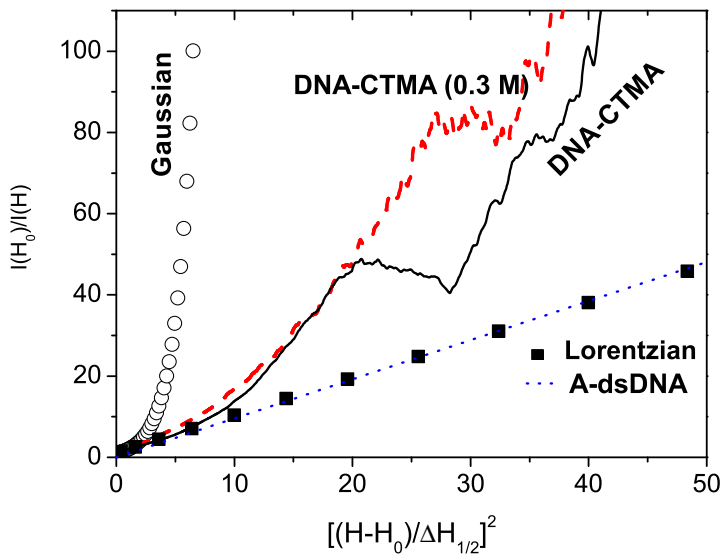


Figure 1.7 $[(H\text{-}H_0)/\Delta H_{1/2}]^2$ vs. $I(H_0)/I(H)$ plots for discriminating a motional dimension of the charge carriers.

transport region, A-DNA are able to easily circumvent the impurity by virtue of their coherent charge transport but surfactant-DNAs is expected not to be so. As a result, the introduction of the external spin species into surfactant-DNAs is more likely to generate scattering centers for the helical charge transport than to bring about susceptibility enhancement. This scenario can be confirmed via an analysis of motional dimension of the charge carriers as shown in Figure 1.7, where DNA-CTMAs are satisfactorily described by a quasi one-dimensional motion evidenced from intermediate position between the Gaussian and the Lorentzian curves in the $[(H\text{-}H_0)/\Delta H_{1/2}]^2$ vs. $I(H_0)/I(H)$ plots[83]. Needless to say, this is more likely to occur in the well ordered region than the disordered ones. For the case of the disordered regions, the helical charge transport itself is thought to be difficult because the long-range helical conformation is not preserved well. Therefore, the concept of the molecular solenoid can be adopted but their inductive coupling is not appropriate for the disordered regions. As a consequence, the conductive electrons or holes are expected to have Pauli susceptibility only.

In conclusion, we found that the lateral separation of dsDNA in DNA^--Q^+ complexes reduces the coherent transverse tunneling of charge carriers between dsDNA, leading to a decrease of cyclotron resonance intensity.

1.3.3 Acknowledgments

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